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(56) Documents Cited

GB 2304110 A **GB 2280194 A** **GB 1508253 A**
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(54) Abstract Title

Radiation-curable Ink Compositions

(57) A vehicle for a hot melt ink-jet ink comprises a radiation curable material. The vehicle is a paste or solid at 20°C (preferably also at 25°C). It has a viscosity of less than 25 centipoise, preferably 12 centipoise, somewhere in the range from 40° to 130°C.

GB 2 336 594 A

RADIATION-CURABLE COMPOSITIONS

The present invention relates to radiation curable compositions suitable for use in the field of hot melt ink-jet printing and other applications.

Hot melt inks for use in ink-jet printing are compositions in which a dye or pigment is admixed with a vehicle which is essentially solid at room temperature but liquid at an elevated temperature at which print heads operate. The main advantage of hot melt inks over ink-jet inks which are liquids at room temperature, is that they solidify rapidly upon contact with the substrate. They are solid at room temperature and thus give a print quality which is essentially independent of the nature of the substrate. Moreover, independent temperature control of the substrate allows control of droplet spreading, again essentially independent of the properties of the substrate. This enables a superior print quality to be achieved than is obtainable with the liquid inks.

Current hot melt inks rely on solidification upon cooling to provide integrity of the print. Therefore, the durability of prints produced by the conventional kind of hot melt system is less than would be optionally desired in some applications.

Hot melt ink-like compositions are also used for modelling prototypes of articles of manufacture. A three-dimensional design produced on a computer aided design (CAD) system is used to control a hot-melt system which is used to "print" a hot melt composition in layers to build-up the complete prototype. The compositions used for this application need to be very hard at room temperature.

On the other hand, radiation-curable ink-jet inks are free-flowing liquids at room temperature. They spread rapidly on contact with the substrate until radiation curing causes "setting" of the ink droplets. As mentioned above, the print quality with such

inks is substrate dependent. It is difficult to control the degree of droplet spread and prevent inter-droplet smear.

A new form of hot melt ink formulation has now been devised which achieves benefits over both hot melt ink-type compositions and radiation curable ink-jet compositions. Thus, the present invention now provides a vehicle for hot melt ink-jet ink, the vehicle comprising a radiation curable material, said vehicle being a paste or a solid at 20°C, preferably also at 25°C and having a viscosity of less than 25 centipoise, preferably 12 centipoise at at least one temperature in the range of from 40°C to 130°C.

Those vehicles according to the present invention are solids (including waxy solids) or pastes at room temperature. They are analogues of conventional hot-melt compositions, except that they are radiation curable. Therefore, they exhibit higher durability than the former. Moreover, if they are printed onto a substrate supported on a heated plattern, the viscosity of the printed droplets can be reduced to a desired degree prior to cooling, to optimise print quality.

Vehicles according to the present invention which are pastes at room temperature may be characterised by their viscosity at 20°C, preferably 25°C.

Vehicles according to the present invention which are pastes preferably have a viscosity of at least 500 centipoise (at a shear rate of 20 s^{-1}) at 20°C, preferably also at 20°C. The latter limit distinguishes the compositions from radiation-curable ink-jet compositions which are low viscosity liquids at room temperature. However, more preferably at 20°C (preferably also 25°C), vehicles according to the present invention have a composition of at least 800 centipoise, more preferably at least 1000 centipoise.

Viscosities are expressed on the assumption that any paste vehicle according to the present invention behaves as a substantially Newtonian liquid. However, where non-Newtonian behaviour is apparent, the viscosity is that measured at a moderately low shear-rate, namely 20 s^{-1} .

The compositions according to the present invention need to be liquid and jettable (i.e. having a viscosity of less than 25 centipoise, preferably 12 centipoise), at the print head temperature, i.e. somewhere in the range of from 40°C to 130°C.

Whether solid, or paste, any vehicle according to the present invention may consist of a single radiation-curable material, or a combination of materials, any or all of which is radiation-curable.

The radiation curable material may in itself be sufficiently viscous to endow the vehicle with the necessary solidity or paste-like viscosity at 20°C, preferably 25°C. However, when the radiation curable material is not sufficiently viscous, a thickener (which may be a single component or combination of components) must be included.

Moreover, thickeners (or components thereof) themselves fall into two separate classes. The first class comprises those substances which are not radiation curable and are not capable of involvement in the curing of the primary radiation curable material.

The second class comprises substances which are in themselves radiation curable, and /or at least capable of involvement in the curing of the primary radiation curable material (e.g. by acting as a cross-linking agent).

Materials which are radiation curable and may constitute the sole, or one of, the component(s) of the radiation curable material and /or thickener substance(s) of the second class fall into one or other of two categories.

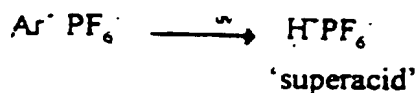
The first category comprises those materials which are curable (i.e. at least capable of involvement in a curing reaction) in the presence of a free radical initiator. The second category comprises those which are curable in the presence of a cationic initiator.

The first category (free radical polymerisable) of materials generally comprises monomers and oligomers having a degree of ethylenic unsaturation, e.g. the (meth) acrylates but preferably they comprise materials having difunctional unsaturated moieties (e.g. vinyl groups) or else have mono-functional unsaturation and must be used in conjunction with separate cross-linking agents in order to allow polymerisation upon curing.

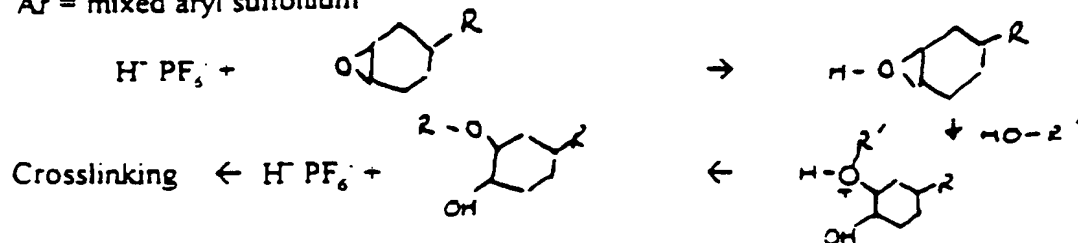
One class of suitable difunctional materials are difunctional acrylates such as a difunctional cycloaliphatic acrylate, for example a difunctional cyclohexane acrylate. A specific material of the latter kind is cyclohexane dimethanol diacrylate sold as CD406X ex Sartomer.

One class of monofunctional materials which are radiation curable and may be used in the presence of a cross-linking agent comprise an acrylate ester of a fatty alcohol or of an ethoxylated fatty alcohol. Suitable examples of such materials are the acrylate esters of Unilin (Trademark) alcohols and of the Unithox (Trademark) ethoxylates ex Petrolite Corp.

Alternatively, cationic curing materials of the second class could be used in place of or together with (so called "hybrid systems") the above mentioned materials of the first class. In these systems crosslinking takes place by an ionic rather than free radical mechanism. One common chemistry used is that of the cycloaliphatic epoxides which cure in the presence of strong cationic initiators. Onium salt photoinitiators are commonly used which undergo photolysis in the presence of uv light to form highly efficient cationic species. A general scheme might be



Ar = mixed aryl sulfonium



Where a radiation curable material (either as primary curable material or as all or part of the thickener) needs the presence of a cross-linking agent to make it sufficiently curable, such cross-linking agent may for example be selected from multifunctional acrylates (for free radical curing systems) and multifunctional epoxides and/or polyols (for cationic curing systems).

Radiation curing, in the context of the present invention means a polymerisation reaction effected by application of any suitable radiation such as electron beam radiation or any appropriate electromagnetic radiation such as in the ultraviolet (UV) spectrum. However, many radiation curable components require the presence of a photoinitiator.

Many suitable materials which are not radiation-curable and may be used as (non-curable) thickeners of the first class are polymeric substances which are hard at room temperature but which becomes liquid at elevated temperatures. Such materials are preferably also film-forming polymers at room temperature, e.g. styrene polymers or copolymers, hydrocarbon resins, phenolic resins and fatty acid amides.

Other materials usable as non-curable thickeners are the urethane oligomers described in PCT Patent Specification No. WO 94/14902. These oligomers are the reaction products of diisocyanates with a monohydric alcohol component, optionally followed by another monohydric component or a dihydric alcohol component followed by a monohydric alcohol component. Another class of suitable such material comprises the urethane- and urea-amides disclosed in our unpublished UK patent application no.

9519646.5. These materials are the reaction products of a mono- or di-isocyanate with one or more functional amides. They typically have molecular weights in the range from 800-1400.

Yet other materials which may typically be used as non-curable thickeners are waxes, typical examples being stearone, carnauba wax, stearyl stearamide, hydrogenated castor oil, erucamide, acid waxes (e.g. Wax S ex Hoechst), ester waxes (e.g. Wax E ex Hoechst, Syncrowax ERLC C₁₈-C₃₆ ester glycol esters, Syncrowax HGLC C₁₈-C₃₆ acid triglyceride ex Croda).

The amount of photoinitiator will normally be from 1%, to 15%, preferably from 1% to 10% by weight of the total composition. A wide spectrum of photoinitiators is commercially available and a non-exhaustive selection of appropriate types include xanthone or thioxanthone types, benzophenone types, quinone types and phosphine oxide types. Sometimes, it is also desirable to include a co-initiator, as well as a primary photoinitiator, most preferably of the amine or aminobenzoate type. In that case, it is preferred for the total photoinitiator (primary initiator plus co-initiator) to be within the aforementioned preferred range. For example, typical co-initiators are aminobenzoate and acrylated amine co-initiators, these generally being used with the xanthone/thioxanthone types of primary photoinitiator. Suitable photoinitiator stabilisers include those disclosed in EP-A-0 465 039.

Generally the vehicle as a whole will make up 50-98% by weight, especially 75-95% by weight of the composition, optionally with one or more optional additives for example, antioxidants, surfactants, levelling additives, photoinitiator stabilisers, wetting agents and pigment stabilisers.

Suitable surfactants are preferably of non-ionic type, for example Fluorad FC430 (ex 3M Corp.). Such surfactants (when present) are preferably included in an amount of from 0.1% to 10% by weight of the total composition.

Hot melt inks can basically be considered to consist of the vehicle plus a colourant optionally with any minor ingredients such as hereinbefore described. The present invention extends to compositions according to the present invention which function as hot melt ink vehicles and those which comprise such a composition according to the present invention together with a colourant, or else otherwise coloured as described hereinbelow.

Broadly speaking, colourants may be considered as falling into two classes, namely dyes, which are substantially soluble in the ink composition, and pigments, which are dispersed in the ink composition in the form of fine particles, if necessary with the aid of a suitable dispersant. The term "colourant" includes materials which endow a non-visible optical property (e.g. fluorescence) to the ink.

Where dyes are employed, these may be selected from a wide range of classes, so long as they are soluble in the ink vehicle. A non-exhaustive list of dyes includes those of the Orasol range ex CIBA and the Savinyl range ex Hoechst. Respectively, typical examples are Orasol blue GN, Yellow 4GN; Savinyl Black RLS and Red GLS.

Pigments may be selected from a wide range of classes, for example, Pigment Red 57:1, Pigment Red 52:2, Pigment Red 48:2, Pigment Blue 15:3, Pigment Green 7, Pigment Yellow 83, Pigment Yellow 13, Pigment White 6, Pigment Black 7. A non-exhaustive list of examples of such pigments include the following from the Irgalite range ex CIBA: Rubine L4, Bordeaux CM, Red 2BP, Blue LG, Green GLN, Yellow B3R and yellow LBG; as well as Tioxide RHD6 (ex Tioxide) and Special Black 250 (ex Degussa).

Where the colourant is a pigment, then unless the pigment is self-dispersing, it is necessary to incorporate a dispersant therefor. Suitable dispersants typically include polyester, polyurethane or polyacrylate types, especially in the form of high molecular weight block co-polymers, and would typically be incorporated at from 2.5% to 150%

by weight of the pigment. Suitable examples are Disperbyk 161 or 162 (ex BYK Chemie) or Solsperse ex Zeneca.

Another way of introducing a colour (or other optical property) is to incorporate an ingredient which itself endows the property, e.g. a polymer or oligomer having a dye moiety bonded onto or incorporated therein. Suitable materials are disclosed in GB-A-2 038 849, US-A-5 264 507, US-1-5 098 475, EP-A- 540 248 and our unpublished UK patent application no. 9520470.7.

The present invention will now be explained in more detail by way of the following description of non-limiting examples.

	Example	1	2	3	4	5	6	7	8
	Form	Solid	Solid	Paste	Paste	Paste	Paste	Paste	Paste
	Viscosity@ 25°C(20s ⁻¹)	Solid	Solid	1000cps	1100cps	1400cps	1300cps	1200cps	1000cps
	Visosity @ 25°C(1000s ⁻¹)	Solid	Solid	~110cps	190cps	~120cps	~120cps	~110cps	~110cps
	Viscosity @ 90°C (1000s ⁻¹)	5.2	5.8	4.1	14cps	4.0	13.0	17.0	15.0
Formulation									
Acrylate ester of Unilin 425									
Alcohol wax X 8505 (1)		21.0	40.0	5.0	5.0	-	-	-	-
Unilin 350 (1)						6.0	-	2.0	3.0
Syncrowax ERLC (4)							5.5	3.0	3.0
Cyclohexane dimethanol diacrylate									
Dipenta erythritol		-	44.8	-	-	-	-	-	-
Pentaacrylate (2) SR 399		-	-	-	10.0	-	-	-	5.0
Ethoxylated neopentyl glycol diacrylate		64.2	-	79.8	64.3	85.6	-	30.0	-
Isobornyl acrylate		-	-	-	-	-	21.0	10.0	30.0

Example	1	2	3	4	5	6	7	8
Form	Solid	Solid	Paste	Paste	Paste	Paste	Paste	Paste
Formulation								
Ethoxylated								
trimethylpropane triacrylate	-	-	-	-	1.5	38.2	37.3	24.0
1,4 butanedrol diacrylate	-	-	-	-	-	20.3	-	20.0
Acrylate Amine CN384 (2)	-	-	-	-	-	5.0	5.0	-
Isopropyl thioxanthone	2.1	2.5	2.5	7.5	1.7	1.5	2.5	1.8
4-phenyl benzophenone	1.0	1.0	1.0	3.0	2.0	1.5	1.0	2.0
2-benzyl-2-dimethylamine-1-(4-morpholinophenyl) butan-1-one	1.0	1.0	1.0	3.0	1.0	0.8	1.0	1.0
(2-ethyl)hexyl	3.0	3.0	3.0	-	2.0	-	-	2.0
4-dimethylamino benzoate								
Fluorosurfactant (Fluorad FC430(3))	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Carbon black	7.5	7.5	7.5	7.0	-	-	-	-
Pigment/Dispersant								

	Example	1	2	3	4	5	6	7	8
	Form	Solid	Solid	Paste	Paste	Paste	Paste	Paste	Paste
Pigment Blue 15:3/Dispersant		-	-	-	-	-	6.0	-	-
Pigment Red 122/Dispersant		-	-	-	-	-	-	8.0	8.0

Total 100%-----

(1) = ex Petrolite Corporation

(2) = ex Sartomer

(3) = ex 3M

(4) = ex Croda

Example	9	10
Form	Paste	Paste
Viscosity @ 25°C (20s ⁻¹)	~3200 cps	~3900 cps
Viscosity @ 25°C (1000s ⁻¹)	~130 cps	~160 cps
Viscosity @ 80°C (1000s ⁻¹)	~16.3 cps	~14.0 cps
CYRACURE UVR 6105 (1) (3,4, Epoxy cyclohexyl methyl-3,4- epoxy cyclohexane carboxylate)	78.8	73.8
CYRACURE UV1 6900 (1) (Mixed triaryl sulfonium Hexafluorophosphate salt)	6.0	6.0
Rapicure HBVE (4-hydroxybutyl vinyl ether)	10.0	15.0
Hoechst Wax E (2)	5.0	-
Unilin 425 (3)	-	5.0
Fluorosurfactant (Fluorad FC 430) (4)	0.2	0.2
Total %=	100	100

- (1) ex Union Carbide
- (2) ex Hoechst
- (3) ex Petrolite
- (4) ex 3M

In the light of this disclosure, modification of the described examples, as well as other examples, all within the scope of the present invention as defined by the appended claims will now become apparent to persons skilled in the art.

CLAIMS:

1. A vehicle for a hot melt ink-jet ink, the vehicle comprising a radiation curable material, said vehicle being a paste or a solid at 20°C, preferably also at 25°C and having a viscosity of less than 25 centipoise, preferably 12 centipoise at at least one temperature in the range of from 40°C to 130°C.
2. A vehicle according to claim 1, wherein said radiation curable material is a paste or a solid at 20°C, preferably at 25°C.
3. A vehicle according to claim 1, further comprising a thickener.
4. A vehicle according to claim 3, wherein the thickener is not radiation curable.
5. A vehicle according to claim 4, wherein the thickener is present at from 0.5% to 30%, preferably from 3% to 10% by weight of the vehicle.
6. A vehicle according to claim 3, wherein the thickener comprises a radiation curable component.
7. A vehicle according to claim 6, wherein the radiation curable component is curable by a free radical initiator.
8. A vehicle according to claim 6, wherein the radiation curable component is curable by a cationic initiator.
9. A vehicle according to any of claims 6-8, wherein the thickener comprises from 0.5% to 80%, preferably from 3% to 10% by weight of the vehicle.
10. A vehicle according to any preceding claim, wherein the radiation curable material is curable in the presence of free radical initiator.

11. A vehicle according to claim 10, wherein the radiation curable material comprises at least one ethylenically unsaturated monomer or oligomer, preferably a (meth) acrylate monomer or oligomer.
12. A composition according to claim 10 or claim 11, wherein the radiation curable material comprises a monofunctional acrylate.
13. A composition according to claim 12, wherein the monofunctional acrylate is an acrylate ester of a fatty alcohol or an ethoxylated fatty alcohol.
14. A composition according to claim 12 or claim 13, which composition further comprises a cross-linking agent.
15. A composition according to claim 10 or claim 11, wherein the radiation curable material comprises a difunctional di-acrylate.
16. A composition according to claim 15, wherein the difunctional di-acrylate is a difunctional cycloaliphatic di-acrylate.
17. A composition according to any of claims 1-9, wherein the radiation curable material is curable in the presence of a cationic initiator.
18. A composition according to any preceding claim, further comprising a photoinitiator.
19. A hot melt ink comprising a composition according to any preceding claim and a colourant.
20. A hot melt ink comprising a composition which comprises one or more materials according to any preceding claim, at least one of said materials being coloured.



Application No: GB 9808480.9
Claims searched: 1-20

Examiner: S.I.Ahmad
Date of search: 27 July 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C4A(AC), C3V (VAE), CEW(W225)

Int Cl (Ed.6): C09D-11/02

Other: Data-base: Cas-on -L

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	JP 06200204 A2 Brother Ind Ltd, Japan	1 at least
X	GB 2304110 A Tioxide Specialities Ltd	"
X	GB 2280194 A Shell Internationale	"
X	GB1508253 A Shering A.G.	"

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.